UDC 666.3.016:666.714

TECHNOLOGICAL PARTICULARITIES OF CLINKER BRICK PRODUCTION

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Translated from *Steklo i Keramika*, No. 4, pp. 17 – 20, April, 2009.

It is determined that raw materials from different deposits can be used to produce clinker ceramic. The rational compositions developed for the mixes are adapted to conventional technology for fabricating brick by plastic molding, and after firing they permit obtaining high-quality clinker articles. A model representing the required ratios of the main oxides in the chemical composition of the ceramic for obtaining clinker brick with prescribed properties and at different firing temperatures is constructed on the basis of the experimental data.

Key words: clinker brick, raw materials, ceramic structure, oxides ratio

The diversity of texture, wide range of colors, high strength and frost-resistance [1, 2], and good aesthetic characteristics of clinker brick make most conventionally used building materials uncompetitive. All this is expanding the applications of this product for facing buildings, reconditioning roads and courts, paving sidewalks, and so forth.

As a rule, the conventional brick technology with plastic molding, drying, and firing at temperatures 1150 – 1240°C is used to manufacture clinker articles. Low- and high-melting clays, which are abundant in nature and inexpensive, serve as the raw material. In recent years it has been proposed that clay from the Ivano-Frankovskoe and Khmelevskoe deposits as well as wastes from the chemical and mining industries be used as a base for ceramic mixes [3 – 5]. It is completely obvious that deeper studies directed toward expanding the raw materials base for manufacturing clinker brick and the influence of these materials on the usage properties of the brick are needed.

The objective of our work is to develop ceramic mixes based on clayey and pegmatite-bearing materials, deposits of which are located in different regions of Ukraine, as well as to determine the effect of the technological parameters on the formation of the structure of a ceramic during firing and therefore on the physical and ceramic properties of the structure. Depending on the territorial location of a particular group of raw materials, the most rational mix compositions are those presented in Table 1.

In view of their ubiquity on the territory of Ukraine, low-melting red-burning clays, loams, argillites, and schists taken from different deposits as well as rock overburden in rock quarries producing kaolin and refractory clays (depending on the region) were investigated to work out the composition of the ceramic mixes. As a rule, however, the sintering interval of the these clayey materials is quite narrow (about 50°C) and fire shrinkage at 950 – 1050°C is elevated, which is due to the substantial content of iron and titanium oxides as well as calcium and magnesium carbonates and sulfates [6]. In addition, because of the formation of a large quantity of a liquid phase starting 900°C it is virtually impossible to obtain densely sintered articles with no deformation. This makes it necessary to introduce additionally into the mixes components which would promote complete sintering in a wider temperature interval, decreasing the shrinkage and en-

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TABLE 1.

Region of Ukraine	Mix composition	Content, wt.%					
		low-melting clay	clayey rock overburden	refractory clay (unconditioned)	kaolin	pegmatitic rock	non-enriched alkali kaolin
Western	I	60 – 70	–	–	–	5 – 15	20 – 30
Northeast	II	60 – 70	–	10 – 20	5 – 15	10 – 20	–
Southeast	III	–	55 – 65	15 – 45	–	0 – 15	–

0361-7610/09/0304-0132

suring that the physical – chemical processes required for the formation of a ceramic occur.

A non-enriched alkaline kaolin, pegmatitic rocks, recovered kaolin, and refractory unconditioned clay taken from different operating quarries were chosen for such components.

Ceramic mixes were prepared by comminution of all components to complete passage through a No. 08 sieve, moistened to 14 – 16%, and carefully mixed. Then, 30 × 30 mm cubic samples were molded by the plastic method and allowed to dry naturally in air at 120°C for 1 day, after which they were fired in an electric furnace. The maximum temperature and soaking time were determined experimentally. Depending on their composition the mixes were held at temperatures 1140 – 1200°C for 1.5 – 2 h. The properties of the best samples obtained from the ceramic mixes belonging to different groups are presented in Fig. 1.

The experimental ceramic samples have quite low water absorption (2.8 – 4.0%) and high compression strength (59 – 67 MPa) and frost-resistance (60 – 68 cycles), which meets the requirements for clinker ceramic. Such high indicators for the main physical – ceramic properties are reached as a result of the completion of high-temperature processes, which promote the formation of a dense structure of the ceramic. The influence of low-melting clays, which have a high content of iron and titanium oxides as well as alkali and alkali-earth metals, predominating in the mix (55 – 70%[3]) is seen in the temperature interval 750 – 900°C. In this complex system they permit the formation of an adequate amount of liquid phase at lower temperatures and, correspondingly, maximum densification of the material [7].

At the same time additives and other components have a large effect on the processes resulting in the formation of ceramic. The central, eastern, and southeast regions of Ukraine have substantial deposits refractory clays, kaolins (including unconditioned), and pegmatitic rocks. It must be underscored that unconditioned clayey materials with more than 2% iron and titanium oxides are almost never used in the production of large quantities of refractories, porcelain, and delftware. However, because of their high plasticity clayey materials improve the molding properties of ceramic mixes for fabrication of articles to be used in construction (mixes II and III). In addition, refractory clay (or kaolin) acts in high-temperature phase transformations as a structure-forming component, which forms a framework that has the required phase composition and resists high-temperature deformation and which makes it possible to obtain a dense ceramic structure without any indications of burning (vitrification or swelling) and deformation in a wide temperature range, as a result of which the manufactured articles remain with the established dimensions.

Pegmatitic rock, being an integral part of a clinker ceramic mix, performs critical functions in the article fabrication technology. At the mix preparation and article formation stages it acts as grog and during firing, especially at temperatures above 1100°C, it is a flux and assists in forming the required amount of liquid phase and attaining the maximum densification of the articles.

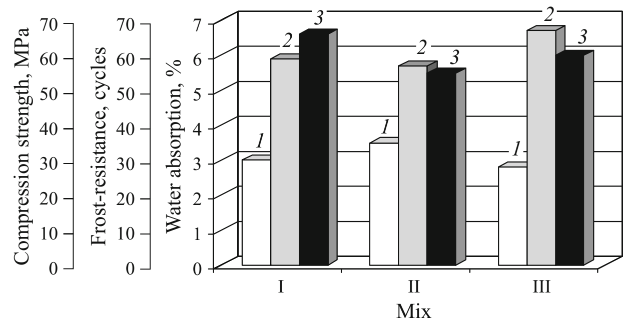

Fig. 1. Main properties of the experimental samples: *1*) water absorption; *2*) compression strength; *3*) frost-resistance.

Substantial deposits of kaolins are found in Western Ukraine. These kaolins are predominately used in the production of fine ceramic. However, if they contain a high content of the colorants iron and titanium oxides (> 2%), they likewise remain unused and dumped into tailings when quarries are put back into production. The introduction of such kaolins into mixes for clinker brick (mix I) turns out to be a positive complex action [8]. In the first place, the refractory components (quartz and kaolinite) present in ceramic mix expand the sintering interval of the mix, which permits the firing process to reach a higher degree of completion and therefore yields a dense structure with a prescribed phase composition. In the second place, the alkali-containing material (microcline) which is present and functions as a flux in the system indicated, activates liquid-phase sintering, which, in turn, makes it possible to obtain sintered articles with low water absorption. Since the content of alkaline kaolin in ceramic mixes is limited because refractory kaolinite is introduced together with it (as the amount of the latter increases, the sintering temperature of the ceramic mix increases), the remaining amount of fluxing agent required is obtained by introducing pegmatitic rock, which contains up to 10% alkali-metal oxides.

It is known [6 – 8] that one of the main factors influencing the formation of the structure of a ceramic material is the chemical composition of the mix. Figure 2 displays the limits of the content of the main oxides in the sintered material such that sintering forms a ceramic with a dense structure, which, in turn, imparts a complex of properties which are required for clinker brick.

So, the following content of oxides (%) is optimal for samples sintered at 1140 – 1150°C: 62.8 – 67.1 SiO_2, 17.5 – 23.2 Al_2O_3, 7.3 – 10.0 $(RO + R_2O)$, 5.45 – 6.10 $(Fe_2O_3 + TiO_2)$. For these ratios a dense, well-sintered ceramic is obtained (Fig. 3*a*). If the content of only of these oxides deviates from optimal value, the phase equilibrium is

[3] Here and below — content by weight.

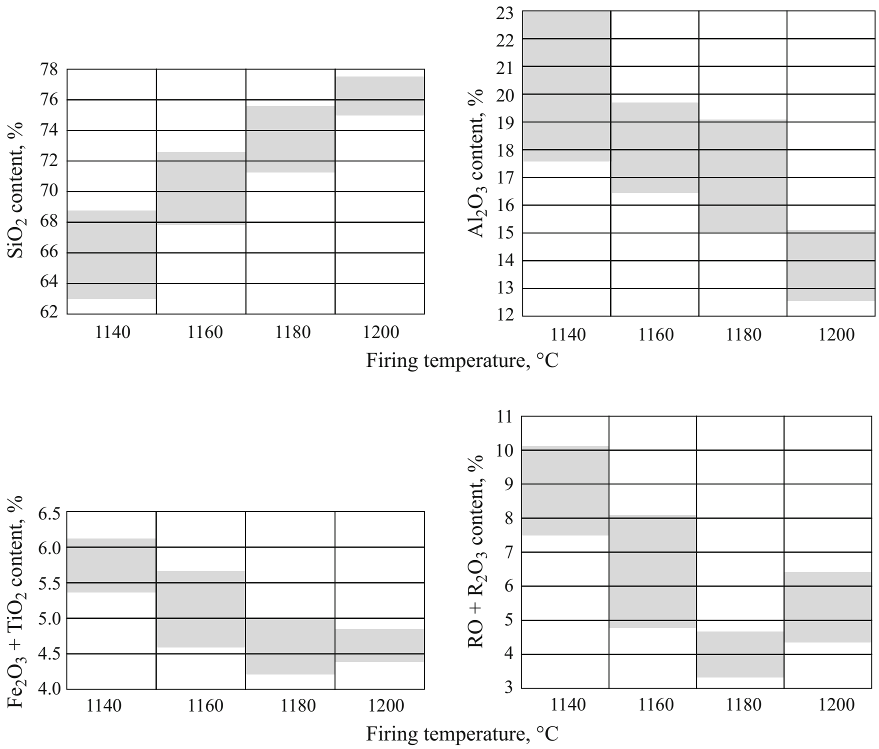

Fig. 2. Regions of optimal content of the main oxides as a function of the sintering temperature of clinker ceramic.

destroyed and as a result the main physical – ceramic indicators decrease. For example, a higher content of iron and titanium oxides (> 6.0%) leads to the formation of low-melting eutectics with the components of the mix and, in consequence, the amount of the liquid phase increases, which results in vitrification of the samples (Fig. 3*b*). For higher SiO_2 content (> 67.0%), a substantial number of microcracks are observed to appear on the surface (Fig. 3*c*), which, in our opinion, are caused, for sufficiently high degree of sintering in the temperature interval 1120 – 1170°C, by volume polymorphic transformations of course-grain silica fractions.

It is known [6, 9] that silica performs an important function in the formation of the structure of a ceramic — at elevated temperatures silica, dissolving in the glassy phase, on the one hand increases the viscosity and on the other hand imparts thermal stability and mechanical strength to the sintered material. However, higher sintering temperatures are required for ceramic mixes with larger amounts of silica.

To prevent an elevated content of a glass phase in the material being sintered at higher temperatures, it desirable to introduce into the mix lower quantities of fluxes, which already at temperatures below 1000°C promote intense formation of a liquid phase.

The results reflecting the need to decrease the Al_2O_3 content in the ceramic mix used for making brick at elevated sintering temperature, which at first glance appear to be contradictory, can be explain as follows. At lower sintering temperatures (1140°C) a high content of finely disperse clayey components is observed in the mix, and it is precisely because of their fineness (< 1 μm) that these components promote sintering of the material. The same components are the main Al_2O_3 “donor” in the mix. At higher temperatures an elevated content of clayey materials will result in deformation of the articles produced. Consequently, other components (pegmatitic rock, alkaline kaolins, and others), which lower the content of the clayey materials, are introduced into the mix.

Petrographic analysis of the experimental samples sintered at 1180°C (Fig. 4) showed that they have identical microstructure. The microstructure is represented by different crystalline phases and a glassy phase, which contains residual quartz grains of different size as well as fragments of fused feldspar grains. The quartz grains have a fissured surface, explainable by the high corrosion power of the feldspar melt, which during sintering at 1180°C interacts intensely with quartz, especially in the sites of defects of its surface.

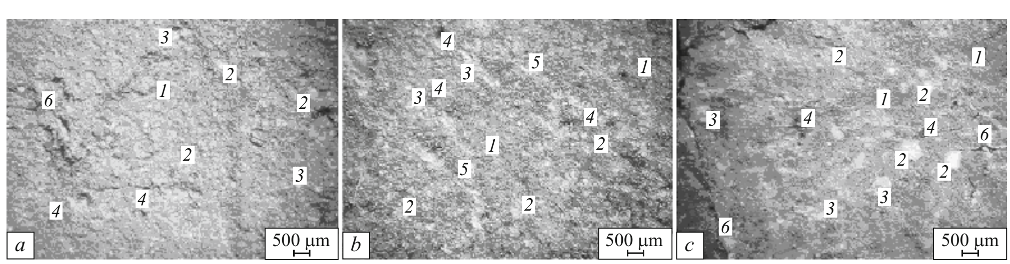

Fig. 3. Microstructure of ceramic samples with different chemical composition (sintering at 1140°C): *a*) optimal ratio of the oxides (densely sintered material); *b*) elevated content of fluxes (vitrified sample); *c*) elevated content of quartz (many cracks, polished section); *1*) main glassy mass; *2*) quartz grains; *3*) feldspar grains (more fused than quartz); *4*) inclusions of iron-bearing minerals; *5*) vitrified sections; *6*) microcracks.

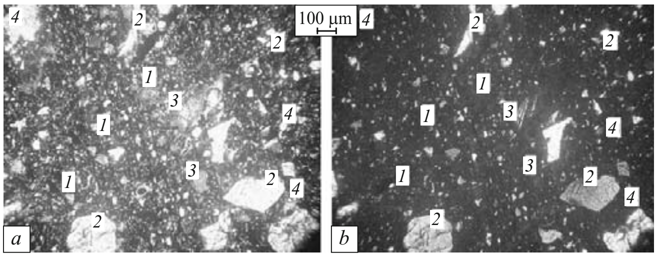

Fig. 4. Fragment of the microstructure of a ceramic sample after sintering at 1180°C (section): *a* and *b*) photographs made without and with an analyzer; *1*) main glassy phase; *2*) quartz grain; *3*) fused feldspar grains; *4*) pores.

The substantial change occurring in the feldspar grains during heat-treatment should be noted. The temperature at which microcline, being one of the main components of pegmatitic rock, starts to melt, is 1150 ± 20°C [9]. However, microcline grains smaller than 50 – 60 μm completely transform into the glassy state during sintering and leave only diffuse contours. Larger grains (about 100 μm) have a wide fusion border (20 – 25 μm) and retain a dual structure at the center, but such grains in samples sintered at 1180°C and above are only encountered in single fragments.

The experimental samples also contain pores of different size (10 – 100 μm) formed as a result of burnup of organic impurities and deposits of carbonate- and sulfate-containing compounds (larger pores) as well as at locations of previously existing feldspar grains (smaller pores).

In summary, it has been shown that clinker ceramic based on local raw material can be obtained. Rational mix compositions adapted to the conventional technology used to manufacture brick by plastic molding have been developed. After sintering they make it possible to obtain high-quality clinker articles.

In addition, a model reflecting the required ratios of the main oxides in the chemical composition of the ceramic material, which ensure that clinker ceramic with prescribed properties is formed at different sintering temperatures, was constructed on the basis of a large amount of experimental data.

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